JOURNAL OF CATALYSIS 60, 378–384 (1979)

Oxygen Isotope Reactions on Platinum

R. P. H. GASSER AND G. J. PERRY

Physical Chemistry Laboratory, University of Oxford, South Parks Road,
Oxford OX1 3QZ, England

Received September 7, 1978

The efficiency of a platinum filament as a catalyst for the oxygen isotope equilibration reaction $^{16}O_2 + {}^{18}O_2 = 2\ {}^{16}O^{18}O$ has been measured for filament temperatures between 300 and 1400°K. The maximum efficiency was about 11% near 950°K. The results are compared with the initial sticking probability of oxygen in the same temperature range and with the rate of the high temperature (>1000°K) pumping action of the filament. It is concluded that the adsorption and isotope equilibration reactions are related but that pumping proceeds by a separate process, although not through thermal accommodation of oxygen on the surface.

INTRODUCTION

The comparative weakness of the bond between a platinum surface and an oxygen atom, $\chi_{Pt-O} = 75$–85 kcal atom^{-1} (*1–4*), imparts an interesting and varied surface chemistry to the system Pt/O_2. The phenomena have been investigated by a wide range of surface techniques, including LEED, AES, XPS, molecular beams, and theoretical calculations. A comprehensive list of references is available (*5*). At room temperature and above the adsorption of oxygen is generally agreed to be atomic (*5*), the evidence coming particularly from kinetic analysis of desorption peaks and isotopic scrambling of adsorbed mixtures of $^{16}O_2$ and $^{18}O_2$ on flash desorption. However, there does not seem to be any evidence about the efficiency of platinum as a catalyst for the equilibration of a mixture of $^{16}O_2$ and $^{18}O_2$ under steady-state conditions. This has, therefore, been measured. An additional significant feature of the interaction of oxygen with platinum is the pumping effect of a hot ($T > 1100$°K) filament on a stream of gas (*6*), an effect which has been attributed to atomization. An interesting question then arises as to the relationships between catalytic activity at high temperatures, adsorption, and the pumping processes. These, too, have now been explored.

The reactivity of a layer of oxygen toward hydrogen (*7–9*) and carbon monoxide (*4, 5*) has been studied under a variety of conditions. It appeared that the steady-state production of carbon dioxide from a stream of carbon monoxide and oxygen passing over a platinum surface depended critically on the P_{CO}/P_{O_2} ratio; a change of mechanism on a polycrystalline sample occurred when this ratio was about 0.6. The temperature of the filament also played an important role in determining the rate of production of carbon dioxide, a significant divide occurring near 550°K. An extension of these studies to the room temperature initial (rather than steady-state) rate of oxidation of carbon monoxide in a stream of $(CO + {}^{18}O_2)$ and to the rate

0021-9517/79/150378-07$02.00/0

of removal of a layer of ^{18}O by CO has been attempted.

EXPERIMENTAL

The Pyrex glass, ultrahigh vacuum apparatus has been described previously (*10*). Gases (B.O.C. Ltd., Research grade) were admitted to the platinum filament (Johnson-Matthey $\nless 99.99\%$, $l = 29.7$ cm, geometric area $= 1.14$ cm^2) through either of two bakable metal valves. The aperture of a similar valve connecting the filament chamber to the pump was adjusted to give a suitable flow rate of gas, and the pumping constant of the setting was measured with nitrogen to avoid the difficulties caused by reversible adsorption on the walls. Mass spectra were recorded with an omegatron radiofrequency mass spectrometer connected to the filament chamber by wide bore tubing. The sensitivity of the omegatron for the various gases was measured by calibration against a Bayard–Alpert gauge, using a lanthanum hexaboride-coated filament for carbon dioxide to minimize thermal decomposition. The manufacturer's quoted sensitivity was used to calculate uptakes, which may, therefore, contain a significant systematic error (*11*). There were two troublesome features to these experiments, the reversible adsorption of carbon monoxide on the walls of the uhv chamber and the adverse effect of oxygen on the performance of the omegatron. These factors limited the range of conditions that could be investigated and the accuracy of the results. Analogous calibration errors of 20 to 30% have been reported (*12*).

The filament was cleaned by extensive heating in oxygen followed by flashing *in vacuo*. This process has been shown to produce an essentially clean surface (*4*, *13*). Filament temperatures were calculated from the room temperature resistance, measured with a Smith's difference bridge, and the literature values of the temperature dependence of resistivity (*14–16*).

The adsorption of oxygen or carbon monoxide was recorded by flashing the filament to about 1400°K for 10 sec in a stream of the gas and then reducing the heating current to give the required filament temperature. The subsequent pressure changes during adsorption of gas were followed mass spectrometrically. Uptake curves (plots of s against θ) were calculated in the usual way from this pressure record. At the highest filament temperatures (>1100°K) the partial pressure of oxygen returned to a steady-state value below the equilibrium pressure. This was the result of the pumping action by the filament (*6*).

Oxygen isotope equilibration was observed by streaming a mixture of approximately equal partial pressures ($P_{\mathrm{total}} \simeq 6 \times 10^{-8}$ Torr) of $^{16}O_2$ and $^{18}O_2$ (Yeda 99.8% ^{18}O) over the filament. The onset of equilibration was marked by the appearance of a peak at mass 34, which grew at the expense of masses 36 and 32. When steady-state conditions had been reached for a chosen filament temperature the peaks at masses 32, 34, and 36 were recorded. The range of filament temperatures was 300 to 1400°K.

The production of carbon dioxide from oxygen and carbon monoxide was observed either by exposure of the oxygenated (with $^{18}O_2$) filament to carbon monoxide ($C^{16}O$) or by passing a mixture of gases ($P_{C^{16}O} \simeq 1.5 \times 10^{-8}$ Torr, $P_{^{18}O_2} \simeq 2.5 \times 10^{-8}$ Torr) over the filament. The former experiment was performed at room temperature, the latter for $300 < T_{\mathrm{fil}} <$ 1400°K.

RESULTS AND DISCUSSION

The adsorption characteristics of oxygen and carbon monoxide were measured as a way of comparing the reactivity of the surface with previously studied polycrystalline samples. The room temperature initial sticking probability of oxygen was 0.18, a value in accord with earlier work (*3*, *9*, *12*), while the maximum room tem-

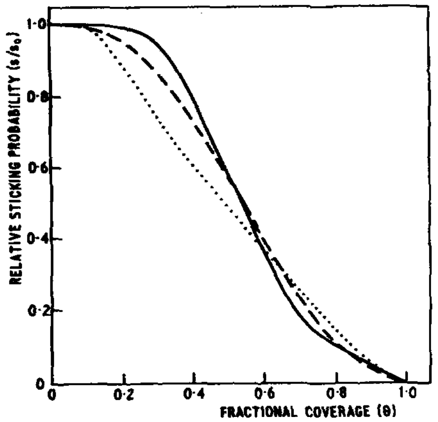

FIG. 1. Comparison of the sticking probability curves of oxygen on a platinum filament (this work ——) with a precursor state theory (– – –) and with an earlier experiment (· · · ·).

perature uptake was about 2.7×10^{14} atom cm^{-2}. Although this value is within the range of earlier reports (*17*, *5*) it may be less than the true uptake as the result of contamination by carbon monoxide released from the walls during the flash (*12*). A sticking probability curve is compared with a precursor state theory of adsorption (*18*), using a site visitation parameter (i.e., the average number of chemisorption sites visited by a molecule in the precursor state) of 3 in Fig. 1, and with a recent uptake curve on a ribbon which had been cleaned by a process similar to that used for the filament (*3*). In view of the possibility that the two samples had different proportions of the two planes produced by heating polycrystalline platinum surfaces [the (100) and (111)], the agreement is reasonable.

The uptake of carbon monoxide at an equilibrium pressure of about 3×10^{-8} Torr and at filament temperatures between 300 and 800°K was measured. The saturation uptake was about 7×10^{14} mol cm^{-2} at room temperature and declined approximately linearly in the temperature range 300 to 600°K. At this latter temperature θ_{max} was about 0.5×10^{14} mol cm^{-2}. These results are entirely in accord with previous observations (*4*, *19–22*). It thus appears that the behavior of this filament toward oxygen and carbon monoxide separately was similar to that of polycrystalline samples studied previously.

OXYGEN ISOTOPE EQUILIBRATION AND PUMPING

The catalytic efficiency of the filament for the reaction

$$^{16}O_2 + {}^{18}O_2 = 2{}^{16}O^{18}O$$

was measured by streaming a mixture of approximately equal partial pressures ($\sim 6 \times 10^{-8}$ Torr total) of the homonuclear isotopes over the filament at a chosen temperature ($300°K < T_{fil} < 1300°K$) and recording the steady-state partial pressures of masses 32, 34, and 36.

The efficiency E (which reflects the probability that collision leads to equilibration) was calculated, as before (*23*), from the expression

$$E = 2k_{34}cV({}^{34}X - {}^{34}X_0)/ AZ(4{}^{32}X{}^{36}X - {}^{34}X^2)$$

in which k_{34} is the pumping constant for $^{16}O^{18}O$, V is the volume of the apparatus, c is a constant relating the number density of molecules to pressure, A is the area of the filament, and Z is the collision rate of oxygen per square centimeter at a pressure of 1 Torr ${}^{i}X$ is the mole fraction of

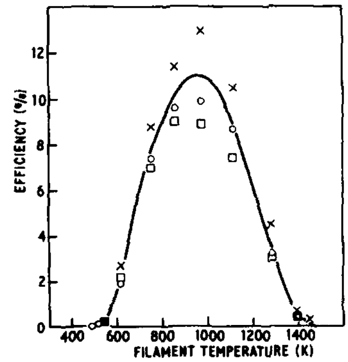

FIG. 2. The efficiency of a platinum filament as a catalyst for oxygen isotope equilibration. Pumping constants (sec⁻1): □, 0.24; ○, 0.28; ×, 0.39.

the species ${}^{i}O_2$ in the gas phase and ${}^{34}X_0$ is the background partial pressure of ${}^{16}O{}^{18}O$ with the filament inactive. In these experiments ${}^{34}X_0$ was zero. As before, the difference in pumping rates of the different isotopes has been ignored; the effect is only ±3% and is well within the scatter. The results of experiments at three flow rates are shown in Fig. 2. As noticed in the hydrogen isotope equilibration reaction on rhodium, there appears to be some dependence of E on k, of, at present, unidentified origin (*10*).

The onset of catalysis above a filament temperature of 500°K matched closely the temperature at which the surface coverage of oxygen began to diminish on this filament (as measured by flash desorption) or on a polycrystalline foil (as measured by AES) (*5*). Similar behavior has been observed previously for nitrogen isotope equilibration on molybdenum (*23*) or rhenium (*24*). The oxygen isotope equilibration results fit into the pattern of adsorption previously proposed. Dissociative adsorption of oxygen would give rise to a layer of atoms, which then combined to desorb as isotopically scrambled molecules only when the filament temperature was high enough to lead to interchange between surface and gas. The reaction would thus proceed by a Langmuir–Hinshelwood mechanism.

At its maximum, near a filament temperature of 950°K, the efficiency was 11%, and the fractional uptake of oxygen was about 0.05. If the postulate of full equilibration on the surface (*24*) is justified, this value of E then corresponds to a "reactive sticking probability" (*24*) of 0.11. The unusual feature of the results was the decline in E to zero at 1400°K. It is more common for a plateau region to be observed at high temperatures or, at most, a modest decline. For example, the reactive sticking probability of carbon monoxide (as measured by isotope equilibration) on rhenium declined from 0.4 at 1300°K to 0.2 at 1800°K. The interpretation of this observation was the failure of statistical equilibrium to be achieved (*24*).

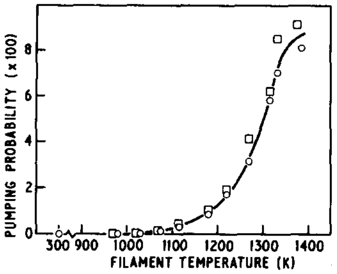

Fig. 3. The probability of pumping of oxygen molecules by a platinum filament. Pumping constants (sec^{-1}): ○, 0.31; □, 0.26.

The pumping of oxygen when the filament was heated above 1100°K caused a diminution in the steady-state pressure, P_∞, below the equilibrium pressure, P_{eq}, observed with the filament inactive. These pressure measurements allow a steady-state, high-temperature pumping probability, S^*, to be calculated from the formula (*25*):

$$S^* = \frac{nkV}{ZA}(P_{eq}/P_\infty - 1).$$

Similarly, the sticking probability on the clean filament, s_0, can be calculated by substituting the minimum pressure obtained from the P vs t record for P_∞. The resulting temperature dependence of S^* is shown in Fig. 3. It should be noted that for filament temperatures in excess of that at which pumping was first observed, $T_{fil} > 1100°K$, the measured value of the initial sticking probability, $(s_0)_{meas}$, may include a contribution from the diminution in pressure brought about by this pumping, as well as by adsorption. If this effect made its maximum contribution, i.e., if S^* were independent of coverage, the true initial sticking probability $(s_0)_{true}$ would be given by

$$(s_0)_{true} = (s_0)_{meas} - S^*.$$

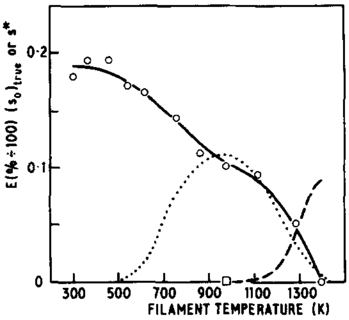

Fig. 4. Comparison of the true initial sticking probability (O), the catalytic efficiency (····), and the pumping probability, S^* (– – –).

To test whether this was so and to relate adsorption to catalytic activity we have plotted in Fig. 4 $(s_0)_{\text{true}}$ and E as functions of filament temperature. As anticipated for an equilibration reaction following a Langmuir–Hinshelwood mechanism, the values of $(s_0)_{\text{true}}$ and E come together in the filament temperature region where the coverage was sparse ($T_{\text{fil}} > 900$°K). Thus, as far as adsorption and catalysis are concerned, we conclude that the sites of activity are closely related. The onset of pumping above a filament temperature of about 1100°K is in good agreement with earlier work (*1*). However, an unusual feature of these results is the monotonic decline of the true adsorption probability on a clean filament from 0.18 at room temperature to zero at 1400°K.

There remains for comment the curious observation that although above 1400°K the filament was not apparently chemisorbing oxygen ($E = s_0 = 0$), it was nonetheless pumping the gas, a process which has been said to take place by atomization (*6*). We are thus led to enquire whether atomization could take place on the surface by thermal accommodation of the adsorbed species between atomic and molecular states, rather than by chemisorption. Were this to lead to roughly 8% dissociation ($S^* = 0.08$) at 1400°K the observations would be rationalized.

In order to make some assessment of the plausibility of this suggestion we shall make an order of magnitude (or perhaps worse) estimate of the degree of dissociation to be anticipated. For the model we take oxygen atoms with two degrees of translational freedom and, for consistency, oxygen molecules with two degrees of translational freedom and one degree of rotational freedom (i.e., parallel to the surface). The additional degree of vibrational freedom will be ignored for simplicity, as will electronic partition functions.

The surface partition functions may now be written as:

$$(Z_{\text{O}_2})_{\text{surf}} = (Z_{\text{O}_2})_{\text{trans.2D}} \times (Z_{\text{O}_2})_{\text{rot.1D}}$$

$$= A\,\frac{(4\pi mkT)}{h^2}\left(\frac{8\pi^2 IkT}{\sigma h^2}\right)^{\frac{1}{2}}$$

$$(Z_{\text{O}})_{\text{surf}} = A\,\frac{(2\pi mkT)}{h^2}$$

in which the symbols have conventional significance, the symmetry number σ is 2, and m is the mass of the oxygen atom. The surface equilibrium constant, in terms of numbers of particles, is given by

$$(K_{\text{N}})_{\text{surf}} = \frac{(n_{\text{O}})^2}{n_{\text{O}_2}}$$

$$= \frac{(Z_{\text{O}})_{\text{surf}}{}^2}{(Z_{\text{O}_2})_{\text{surf}}}\exp(-D_0/RT),$$

where D_0 is the dissociation energy of the oxygen molecule, 493.5 kJ mol⁻¹.

Thus

$$(K_{\text{N}})_{\text{surf}} = \frac{A\pi mkT}{h^2}\left(\frac{h^2}{4\pi^2 IkT}\right)^{\frac{1}{2}}$$

$$\times\exp(-493{,}500/RT).$$

In terms of surface concentrations, $c_i = n_i/A$, we can write

$$(K_{\text{C}})_{\text{surf}} = \frac{(C_{\text{O}})^2}{C_{\text{O}_2}}$$

$$= \frac{\pi mkT}{h^2}\left(\frac{h^2}{4\pi^2 IkT}\right)^{\frac{1}{2}}\exp(-493{,}500/RT).$$

Therefore

$$(K_C)_{\text{surf}} = \frac{m}{2h}\left(\frac{kT}{I}\right)^{\frac{1}{2}} \exp(-493{,}500/RT).$$

Now $I = mr^2$, therefore

$$(K_C)_{\text{surf}} = \frac{(mkT)^{\frac{1}{2}}}{2rh} \exp(-493{,}500/RT).$$

Substituting $m = 2.657 \times 10^{-26}$ kg, $k = 1.38 \times 10^{-23}$ J K^{-1}, $T = 1400$°K, $r = 1.207 \times 10^{-10}$ m, $h = 6.626 \times 10^{-34}$ J sec, and $R = 8.314$ J mol^{-1} K^{-1} yields:

$$(K_C)_{\text{surf}} = 54 \text{ particles m}^{-2}.$$

This surface equilibrium constant may be compared with the gas phase equilibrium constant of about 10^{-6} at. at 1400°K. The value of $(K_C)_{\text{surf}}$ can now be used to estimate the surface concentration of adsorbed species ρ at which 8% dissociation (corresponding to a pumping probability of 0.08) would occur. Under these circumstances, the mole fraction of oxygen atoms may be taken as 0.08 and of oxygen molecules 0.92. Then:

$$(K_C)_{\text{surf}} = \frac{(\rho X_O)^2}{\rho X_{O_2}} = 7 \times 10^{-3}\,\rho$$

or

$$\rho \simeq 8000 \text{ particles m}^{-2}.$$

This surface concentration is so low (roughly 1 particle on the experimental filament) that we can discard the hypothesis of a pumping mechanism based on a purely physical process.

It therefore seems that we must look to the extreme range of the possibilities associated with migration-limited bimolecular kinetics in the chemisorbed layer (*24*) for an interpretation. Thus, under circumstances where the filament was sparsely covered, and dissociative chemisorption was followed either (i) by recombination of the atoms with their original partners and desorption, or (ii) by desorption of atoms in a time short compared with that required to find a new partner by migration over the surface, pumping but not isotope equilibration would be observed. In effect, it is suggested that the combination of a low surface coverage (associated with a high filament temperature) and a high activation energy for migration over the surface may cause the bimolecular equilibration process to lose out progressively to unimolecular, atomic desorption. An indication in support of this interpretation comes from the relative immobility of oxygen atoms on platinum. For example, kinetic analysis of desorption pressure bursts indicates a lack of mobility of oxygen on platinum at 700°K (*1*).

REACTION BETWEEN CARBON MONOXIDE AND OXYGEN

The possibility that carbon monoxide may dissociate on platinum (*27*), especially at steps (*28*), has been raised, though this is probably by no means a general occurrence (*29*). To investigate this point further the production of carbon dioxide was recorded either when a layer of oxygen (^{18}O) on platinum was exposed to carbon monoxide ($C^{16}O$) or when a mixture of oxygen and carbon monoxide passed over the filament.

In the replacement reaction, which took place at room temperature, $C^{16}O^{18}O$ was by far the most important product throughout the reaction. The other carbon dioxide species $C^{16}O_2$ and $C^{18}O_2$ were recorded with peaks about 10% of the mixed isotope. However, the proportion of these gases declined when high flow rates were used and their presence can confidently be attributed to secondary equilibration of $C^{16}O^{18}O$ generated at the filament, by oxidized nickel-containing alloys in the metalwork of the uhv system (*30*). These observations are not consistent with a fully dissociative adsorption of carbon monoxide, since the build-up of surface ^{16}O from $C^{16}O$ as the surface coverage of carbon monoxide increased would have led to more $C^{16}O_2$ being produced from dissociated $C^{16}O$. No such change in mass peaks was observed. The temperature dependence of the rate of oxidation (by $^{18}O_2$) of carbon monoxide ($C^{16}O$) under flow conditions was measured by the production of $C^{16}O^{18}O$. The filament was flashed to 1400°K in a stream of gas ($P_{CO} \simeq 1.5 \times 10^{-8}$ Torr, $P_{O_2} \simeq 2.5 \times 10^{-8}$ Torr) and cooled to the chosen temperature. For filament temperatures below 800°K, significant poisoning of the filament occurred, as shown by the decline in the partial pressure of $C^{16}O^{18}O$ with increased exposure. It was, therefore, impossible to obtain a quantitative estimate of the uninhibited activity. However, qualitatively a marked diminution in the initial activity was observed when the filament was above 800°K. These observations accord with earlier reports of blockage of oxygen sites by continued exposure to carbon monoxide (*31*) and with the formation of "nonreactive" oxygen at high filament temperature (*5*).

ACKNOWLEDGMENTS

We thank the Science Research Council for financial support and Professors J. S. Rowlinson and G. Haller for interesting discussions.

REFERENCES

1. Peng, Y. K., and Dawson, P. T., *Canad. J. Chem.* **52**, 3507 (1974).
2. Wilf, M., and Dawson, P. T., *Surface Sci.* **65**, 399 (1977).
3. Alnot, M., Fusy, J., and Cassuto, A., *Surface Sci.* **72**, 467 (1978).
4. Nishiyama, Y., and Wise, H., *J. Catal.* **32**, 50 (1974).
5. Matsushima, T., Almy, D. B., and White, J. M., *Surface Sci.* **67**, 89 (1977).
6. Fusy, J., Webster, B., and Cassuto, A., *J. Chim. Phys.* **66**, 708 (1969).
7. Collins, D. M., Lee, J. B., and Spicer, W. E., *J. Vacuum Sci. Technol.* **13**, 266 (1976).
8. Ducros, R., and Merrill, R. P., *Surface Sci.* **55**, 227 (1976).
9. Alnot, M., Fusy, J., and Cassuto, A., *Surface Sci.* **57**, 651 (1976).
10. Edwards, S. M., Gasser, R. P. H., Green, D. P., Hawkins, D. S., and Stevens, A. J., *Surface Sci.* **72**, 213 (1978).
11. Hayward, D. O., King, D. A., and Tompkins, F. C., *Proc. Roy. Soc.* (*London*) **A297**, 321 (1967).
12. Hopster, H., Ibach, H., and Comsa, G., *J. Catal.* **46**, 37 (1977).
13. Pacia, N., Cassuto, A., Pentenero, A., and Weber, B., *J. Catal.* **41**, 455 (1976).
14. Touloukian, Y., *Thermophys. Props. Matter* **1**, Purdue U.P. (1970).
15. White, G. K., and Woods, S. B., *Phil. Trans. Roy. Soc.* **A251**, 273 (1959).
16. Powell, R. W., Tye, R. P., and Woodman, M. J., *J. Less Common Metals* **12**, 1 (1967).
17. Wood, B. J., Endow, N., and Wise, H., *J. Catal.* **18**, 70 (1970).
18. Gasser, R. P. H., and Smith, E. B., *Chem. Phys. Lett.* **1**, 457 (1967).
19. McCabe, R. W., and Schmidt, L. D., *Surface Sci.* **65**, 189 (1977).
20. Collins, D. M., and Spicer, W. G., *Surface Sci.* **69**, 85 (1977).
21. Kawasaki, K., Kodama, T., Miki, H., and Kioka, T., *Surface Sci.* **64**, 349 (1977).
22. Comrie, C. M., and Lambert, R. M., *J. Chem. Soc. Faraday Trans. I* **72**, 1659 (1976).
23. Gasser, R. P. H., Hale, A., and Marsay, C. J., *Trans. Faraday Soc.* **63**, 1789 (1967).
24. Yates, J. T., Jr., and Madey, T. E., *J. Chem. Phys.* **51**, 334 (1969).
25. Gasser, R. P. H., and Marsay, C. J., *Surface Sci.* **20**, 107 (1970).
26. Thermodynamic Properties of the Elements, Advances in Chemistry No. 18, American Chemical Society, 1956.
27. Bain, F. T., Jackson, S. D., Thompson, S. J., Webb, G., and Willcocks, E., *J. Chem. Soc. Faraday Trans. I* **72**, 2516 (1976).
28. Somorjai, G. A., *Surface Sci.* **34**, 156 (1973).
29. Palmer, R. L., and Smith, J. N., Jr., *J. Chem. Phys.* **60**, 1453 (1974).
30. Conner, W. C., and Bennett, C. O., *J. Catal.* **41**, 30 (1977).
31. Bonzel, H. P., and Ku, P., *J. Vacuum Sci. Technol.* **9**, 663 (1972).